

# ON THE RAMAN SPECTRA OF SOLUTIONS OF 1, 2, 3-TRICHLOROPROPANE\*

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**ABSTRACT.** The Raman spectra of solutions of 1, 2, 3-trichloropropane in methyl alcohol, cyclohexane and dioxane have been investigated and microphotometric records of the spectrograms have been reproduced. It has been found that the line  $872\text{ cm}^{-1}$  of 1, 2, 3-trichloropropane diminishes in intensity greatly when the liquid is dissolved in dioxane. In the case of the solution in methyl alcohol also the intensity of the line seems to be slightly smaller than that in the case of the pure liquid. In the case of the solution in cyclohexane no such changes in intensity are observed. The line  $83\text{ cm}^{-1}$  also diminishes in intensity with dissolution of the substance in dioxane. In the case of *o*-chlorotoluene the intensity of the line  $164\text{ cm}^{-1}$  is found to diminish appreciably when the liquid is dissolved in benzene to make a dilute solution but no such diminution is observed in the case of solutions in either acetone or methyl alcohol.

## INTRODUCTION

It was reported previously (Hariharan, 1952) that the intensity of the line  $162\text{ cm}^{-1}$  of benzoylchloride diminishes to a large extent when the liquid is dissolved in benzene. The Raman spectra of solutions of a few other liquids in different solvents were next investigated and it was found that of these, solutions of 1, 2, 3-trichloropropane yielded some interesting changes. The results have been discussed in the present paper.

## EXPERIMENTAL

The liquids chosen in the present investigation are *o*-chlorotoluene and 1, 2, 3-trichloropropane which were supplied by Eastman Kodak Co., U. S. A. They were distilled in vacuum before use. The solvents were also of chemically pure quality and were distilled in vacuum. The Raman spectra of the pure liquids *o*-chlorotoluene and 1, 2, 3-trichloropropane and of the solutions of the former in benzene, methyl alcohol, and acetone and of the latter in cyclohexane, methyl alcohol and dioxane were photographed with a Fuess glass spectrograph having a dispersion of 12.5 A.U. in the 4000 A.U. region. The Wood's tube containing the solution was provided with an outer jacket containing a dilute solution of sodium nitrite which

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cut off all radiations of wavelengths shorter than 3800 Å. U. This removed the continuous fluorescence which was observed in the case of solutions if no such filter was used. Ilford Zenith plates were used for photographing the spectra and they were developed under identical conditions. Microphotometric records of some of the spectrograms were taken with a Moll type self-recording microphotometer.

The depolarisation of the Raman lines of pure 1, 2, 3-trichloropropane was also studied by photographing the horizontal and vertical components of the scattered light simultaneously using a Wollaston's prism of quartz. As light from a mercury arc focussed with a condensor was used as incident light, the spectrogram did not give the correct values of  $\rho$ , the factor of depolarisation, but to get an estimate of the errors due to convergence and

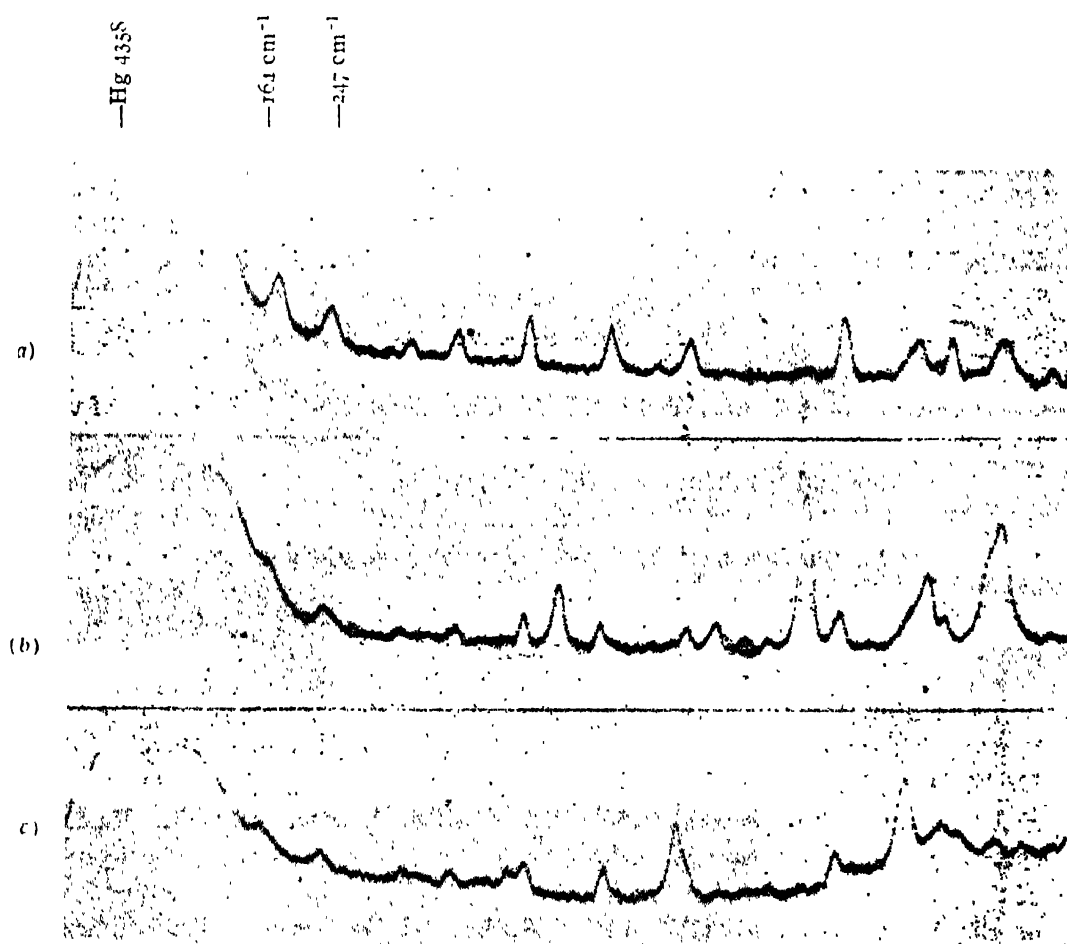


FIG. 1

Microphotometric records of Raman Spectra of *o*-chlorotoluene.

- (a) Pure liquid at room temperature
- (b) Solution in benzene (1:4 by volume).
- (c) Solution in acetone (1:4 by volume).

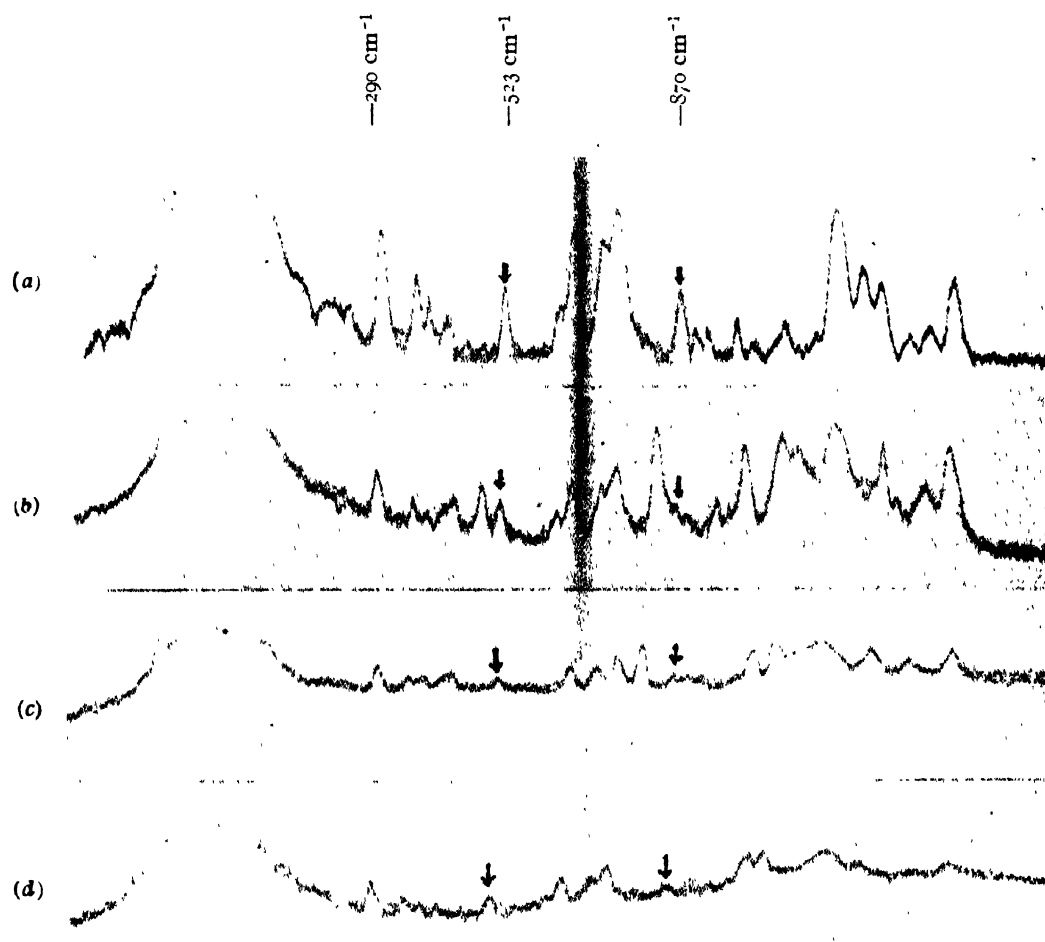


FIG. 2

Microphotometric records of the Raman spectra of 1, 2, 3-trichloropropane

- (a) Pure liquid at room temperature.
- (b) Solution in dioxane, 30% by volume.
- (c) Solution in cyclohexane, 30% by volume.
- (d) Solution in methyl alcohol, 30% by volume

loss due to reflection at surfaces inside the spectrograph, the depolarisation of the Raman lines of carbon tetrachloride was studied under similar conditions and from a knowledge of the approximate values of  $\rho$ , thus found, and of its true value, the correct values of  $\rho$  in the case of the other liquids were estimated.

## RESULTS

The preliminary examination of the spectrograms revealed the fact that the intensities or positions of the Raman lines of *o*-chlorotoluene do not change markedly when the liquid is dissolved in either methyl alcohol or

acetone, but the line  $164\text{ cm}^{-1}$  seemed to be a little weaker in the case of the solution in benzene than in the case of the pure liquid, as can be seen from the microphotometric records reproduced in figure 1.

TABLE I  
Raman spectra of 1, 2, 3-trichloropropane.

Pure liquid at 28°C		Solution in dioxane	Solution in cyclohexane
Present author	Kohlrausch and Ypsilanti (1936)		
83 (2) e, k, $\pm$ D		83 (o) e	83 (o) e
104 (1) e, k, D ?		140 (o) e	140 (o) e
176 (1) e, P		176 (o) e	176 (o) e
187 (1) e, P	188 (o)	187 (o) e	187 (o) e
230 (1) e, k, P	227 (o)	230 (o) e	230 (o) e
290 (10) $\pm$ e, k, i, P	288 (5)	290 (5) $\pm$ e, k	290 (8) $\pm$ e, k
356 (4) e, k, P	356 (2)	356 (2) e	356 (3) e
386 (2) e, P	381 (1)	386 (1) e	386 (3) e
418 (2) e, P	412 (1)	418 (1) e	
			422 (3b) e
523 (4) e, k, D	510 (3)	436 * (4) e	
632 (1) e	628 (1)	523 (3) e, k	523 (3) e
668 (10) $\pm$ e, k, P	660 (6)	632 (1) e	
718 (4) e, k, P	716 (4)	668 (5) $\pm$ e, k	668 (8) $\pm$ e, k
752 (10b) e, k, D	746 (8)	718 (3) e, k	718 (3) e
		752 (6) e, k	752 (8) e, k
872 (4) e, k, D	863 (2)	835 * (10) e, k	801 * (10) e, k, i
906 (1) e, P	906 (o)	872 (o) e	872 (2) e
933 (1) e, P	931 (o)	906 (o) e	
995 (2) e, P	990 ( $\frac{1}{2}$ )	995 (o) e	995 (1) e
1004 (1b) e, P	1090 ( $\frac{1}{2}$ )	1015 * (12) e, k, i	1029 * (8) e, k
1190 (3b) e, k, P	1198 (2)		
1280 (5) e, k, P	1283 (3)	1106 * (6) e, k	1190 (2) e
		1100 (2b) e, k	1267 * (10) e, k
1346 (1) e, P	1338 (1)	1280 (1) e	
1438 (6b) e, k, D	1432 (3b)	1304 * (10) e, k	
		1346 (2) e, k	1438 (10b) e, k
		1438 (10) e, k	1660 * (2) e, k
2799 (1) e, k, D		2660 * (1) e	2689 * (1) e, k
2860 (1) e, k, P	2860 * (2)	2718 * (2) e	2799 * (3) e, k
		2800 * (5) e	2860 * (10) e, k
		2860 * (5) e, k, i	
		2888 * (3) e	
2960 (10b) e, k, i, P	2960 (10b)		2925 * (10) e, k, i
3014 (3) e, k, D	30.8 (6)	2960 (10b) e, k, i	2935 * (10) e, k, i
		3014 (1) e	2960 (8) e, k
			3014 (2) e

N. B. Lines marked with asterisks are due to the solvents.

In the case of 1, 2, 3-trichloropropane, however, some changes were observed in the spectra with the dissolution of the substance in different solvents. The microphotometric records of the Raman spectra of the pure liquid and its solutions are reproduced in figure 2 to show these changes. The lines observed are given in Table I. The nature of polarisation of the

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lines obtained are shown by letters P and D indicating values of  $\rho$  less than and equal to  $6/7$  respectively in Table I in which the data have been tabulated.

### DISCUSSION OF RESULTS

It can be seen from a comparison of figures 2(a) and 2(b) that the relative intensities of the lines  $523$  and  $872\text{ cm}^{-1}$  are almost the same in the case of pure 1, 2, 3-trichloropropane while the latter line is much less intense than the former line in the case of the solution of the liquid in dioxane. A comparison of figures 2(c) and 2(d) also shows that the two lines mentioned above are of the same intensity in the case of the solution in cyclohexane while in the case of solution in methyl alcohol again the line  $872\text{ cm}^{-1}$  is less intense than line  $523\text{ cm}^{-1}$ . In comparison with the intensities of the other prominent lines, e. g., the line  $290\text{ cm}^{-1}$ , the intensity of the line  $523\text{ cm}^{-1}$  is found to remain the same in the solutions in the three different solvents. It is, therefore, evident that the intensity of the line  $872\text{ cm}^{-1}$  diminishes markedly when the liquid is dissolved in either dioxane or methyl alcohol.

As can be seen from Table I, the line  $872\text{ cm}^{-1}$  has a factor of depolarisation of the order of 0.87 while the line  $1438\text{ cm}^{-1}$  is also totally depolarised. Probably the line  $872\text{ cm}^{-1}$  is due to a mode of vibration of the group C-C-C, and the diminution of the intensity of this line probably indicates that the line is not due to a single molecule. As Bishui (1952) has shown that all the lines of 1, 2, 3-trichloropropane persist when the liquid is solidified and cooled down to  $-180^{\circ}\text{C}$  the question of co-existence of two isomeric forms in the liquid state does not arise. The line  $872\text{ cm}^{-1}$  therefore, may be due to some form of associated molecule, the number of which diminishes when the liquid is dissolved in either dioxane or methyl alcohol, but the solvent cyclohexane has no such effect. Visual examination of the spectrograms show that the line  $83\text{ cm}^{-1}$  also diminishes appreciably in intensity when the liquid is dissolved in dioxane.

The 1, 2, 3-trichloropropane molecule cannot have any element of symmetry. The fact that the line  $1438\text{ cm}^{-1}$  is totally depolarised, therefore, indicates that it is the symmetry of the two  $\text{CH}_2$  groups, the deformation C-H oscillation in which gives rise to this line, that determines the polarisation of the line and not the symmetry of the whole molecule.

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